

## Polymer-Supported Metallocene Catalysts for Gas-Phase Ethylene Polymerization

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**Abstract**—The use of hydroxylated chloromethylated-styrene/divinylbenzene copolymer as a support for three different catalysts,  $\text{Cp}_2\text{ZrCl}_2$ ,  $[\text{Ind}]_2\text{ZrCl}_2$  and  $(\text{CH}_3)_2\text{Si}[\text{Ind}]_2\text{ZrCl}_2$  has been examined for the polymerization of ethylene in gas phase. The gas phase polymerization experiments were performed in a horizontal reactor by using Box-Behnken experimental design [Box and Wilson, 1951] to study the effects of temperature, ethylene partial pressure, and MAO cocatalyst level on polymerization. The measured average catalyst activities were empirically correlated with these three factors. Temperature appears to be the most important factor, which shows a first and second order effect on activity and also interacts with pressure and MAO. The kinetic study shows that these supported catalysts might contain two types of active sites, and the deactivation of sites follows a first order kinetic.

Key words: Polymer Supported, Metallocene, Gas Phase Ethylene Polymerization

### INTRODUCTION

Polyethylene (PE) is a commodity plastic material and its production is well over 50 million tons per year world wide. In the past, production processes usually involved free radical polymerization for low density PE, and in using Phillips chromium catalyst for PE of broad molecular weight distribution and Ziegler-Natta catalysts for linear low density PE. The discovery of metallocene catalysts in the early 1980's opened a new era for PE production. There are a number of advantages to using metallocene catalysts. The catalysts are highly active and produce polymer with narrow molecular weight distribution. By manipulating the metallocene compound structure one can produce polymer with tailor-made structure for specific applications.

Metallocene catalysts are basically homogeneous in nature. Many industrial applications require the catalyst to be supported on a carrier. The most commonly used support is  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ , as reported by Soga and Kaminaka [Soga and Kaminaka, 1992, 1994]. However, there are other possibilities, such as the use of polymer as a support.

The control of polymer particle morphology is an important aspect of PE production for practical purposes. The use of polymer as support can facilitate the control of particle morphology without involving a prepolymerization step. It also reduces inorganic residues in the final products. Furthermore, manipulating the functional groups in polymer support opens the possibility of influencing the molecular structure of the polymer. In this study, we have explored the possibility of using hydroxylated styrene/divinylbenzene copolymer as a support for three different metallocene catalysts,  $\text{Cp}_2\text{ZrCl}_2$ ,  $[\text{Ind}]_2\text{ZrCl}_2$  and  $(\text{CH}_3)_2\text{Si}[\text{Ind}]_2\text{ZrCl}_2$  in the polymerization of ethylene in

gas phase, and studied the effects of temperature, monomer partial pressure, and MAO level on polymerization. The polymerization kinetics was also studied by analyzing the polymerization rate data using single-site and two-site models with first and second order catalyst decay.

### EXPERIMENTAL

A detailed description of the procedures for the preparation of polymer support and polymer-supported catalysts, and for the polymerization experiments is provided in [Chung and Hsu, 2002] and [Tairova et al., 1999]. Briefly, the 2% cross-linked chloromethylated styrene/divinylbenzene was first treated with KOH solution at 85 °C to replace chlorine with hydroxyl group. The IR analysis of the treated compound showed a complete disappearance of the absorption peak of chloromethylated benzene at  $1,264\text{ cm}^{-1}$ , indicating a complete replacement of chlorine with hydroxyl group.

In preparing the supported catalyst, we first treated the polymer support with MAO in the presence of toluene and a small amount of heptane at 50 °C for 20 hr. The MAO treated support was recovered by filtration, washing and drying. The solids were then reacted with catalysts at 40 °C for 6-10 hr in toluene. The average zirconium content in catalyst was found to be 0.17% by weight.

The polymerization experiments were performed in a horizontal stirred-bed reactor (10.2 cm dia × 10.2 cm length), made of stainless steel. Purified table salt served as the fluidized bed. The reactor was operated in a semi-batch mode. By maintaining the reactor at a constant pressure, the polymerization rate was measured as the flow rate of monomer entering the reactor. The polymerization rates were recorded as a function of time on an on-line personal computer. For each experiment 120 points were collected in a period of 120 minutes. Box-Behnken experimental design was used to carry out the experimental program for the study of the effects of temperature, ethylene partial pressure, and MAO level on polymerization. A total of 15 experiments were carried out for each catalyst, of which Runs 13, 14, and 15 were experiments of duplicated runs for the analysis of experimental errors. The experimental conditions for these 15

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\*This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

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experiments are given in Table 2, where the 1, 0, and -1 imply three-level design for the polymerization. The measured average catalyst activities in terms of polymerization rate in kg-PE/g-Zr/hr/atm were correlated with these three factors by using a linear second order equation.

In the kinetic study, four models—single-site first-order catalyst decay, two-site first-order catalyst decay, single-site second-order catalyst decay, and two-site second-order catalyst decay—were used to fit the polymerization data.

## RESULTS AND DISCUSSION

The general characteristics of the polymerization rate profile are shown in Fig. 1, where the Experimental Run No. 1 is used as an example for these three catalysts. The experimental conditions for these runs are given in Tables 1 and 2. The profiles of other runs, more or less, give roughly the same shape of curves. They all show a high initial polymerization rate, but decay quickly to a stable level.

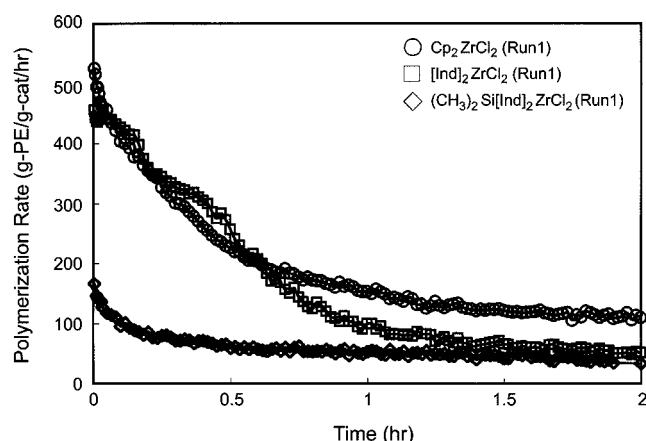


Fig. 1. Typical experimental rate profiles for the gas-phase polymerization of ethylene: Polymerization conditions for run 1: temperature=60 °C, MAO=5 mmol (2.5 mmol for Me<sub>2</sub>Si[Ind]<sub>2</sub>ZrCl<sub>2</sub> catalyst system), ethylene pressure=4 atm.

Table 1. Box-Behnken experimental design for three factors

Run number	X1	X2	X3
1	-1	-1	0
2	1	-1	0
3	-1	1	0
4	1	1	0
5	-1	0	-1
6	1	0	-1
7	-1	0	1
8	1	0	1
9	0	-1	-1
10	0	1	-1
11	0	-1	1
12	0	1	1
13	0	0	0
14	0	0	0
15	0	0	0

Table 2. Polymerization conditions for the three catalysts

	Temperature (X1, °C)			MAO (X2, mmol)			Pressure (X3, atm)		
	1	0	-1	1	0	-1	1	0	-1
Cp <sub>2</sub> ZrCl <sub>2</sub>	80	70	60	15	10	5	6	4	2
[Ind] <sub>2</sub> ZrCl <sub>2</sub>	80	70	60	15	10	5	6	4	2
Me <sub>2</sub> Si[Ind] <sub>2</sub> ZrCl <sub>2</sub>	80	70	60	10	5	2.5	6	4	2

In general, the catalyst (CH<sub>3</sub>)<sub>2</sub>Si[Ind]<sub>2</sub>ZrCl<sub>2</sub> shows a lower initial rate, but it decays to about the same final level. In some cases they exhibit a short induction period where the rate increases quickly to a maximum before it decays. The maximum usually occurs at about 10 to 20 minutes of polymerization.

A linear second order equation was used to correlate the average catalyst activity A in terms of kg-PE/g-Zr/atm/hr with temperature T in °C, pressure P in atm, and MAO level M in mmol. The terms, which are not statistically significant, have been dropped. Their results are given below:

### Cp<sub>2</sub>ZrCl<sub>2</sub>:

$$A = -1.1064(\pm 0.4886)T + 25.4295(\pm 7.7546)P - 0.3893(\pm 0.1103)TxP + 0.0894(\pm 0.0236)TxM + 0.0151(\pm 0.001)T^2 - 0.3199(\pm 0.0818)M^2 \quad (1)$$

### [Ind]<sub>2</sub>ZrCl<sub>2</sub>:

$$A = 0.4947(\pm 0.0910)T - 0.0050(\pm 0.0015)T^2 - 0.4267(\pm 0.2507)P^2 + 0.0117(\pm 0.0078)M^2 + 0.0290(\pm 0.0289)TxP \quad (2)$$

### (CH<sub>3</sub>)<sub>2</sub>Si[Ind]<sub>2</sub>ZrCl<sub>2</sub>:

$$A = -2.7220(\pm 2.2050)M + 0.0646(\pm 0.0404)TxP + 0.1161(\pm 0.0366)TxM - 0.8100(\pm 0.3761)P^2 - 0.3330(\pm 0.1524)M^2 \quad (3)$$

The above correlations indicate that in the ranges of polymerization conditions studied, temperature appears to be the most important factor influencing the average polymerization rate. With the exception of (CH<sub>3</sub>)<sub>2</sub>Si[Ind]<sub>2</sub>ZrCl<sub>2</sub>, the temperature shows a first and a second order effect and its interactions with pressure and MAO. It does not mean that polymerization mechanism of this catalyst is different from other two catalysts. In (CH<sub>3</sub>)<sub>2</sub>Si[Ind]<sub>2</sub>ZrCl<sub>2</sub> system the first and second order effects of temperature are insignificant, but the temperature strongly interacts with pressure and MAO. In [Ind]<sub>2</sub>ZrCl<sub>2</sub> catalyst system, even though the first and second order effects of temperature appear in the correlation, its effect is relatively weak compared to the other two catalysts, a phenomenon that cannot be explained easily.

The effect of partial pressure of ethylene on polymerization is rather complicated. For the catalysts tested, the pressure seems to have a negative effect on rate, i.e., the lower the pressure the higher the rate, which raises the question of whether or not the reaction is a simple first order with respect to ethylene partial pressure (Note that the polymerization rate is in terms of g-PE/g-Zr/atm of monomer pressure/hr). However, the pressure effect is normally weak. MAO level in general does not affect the polymerization much in the range of study. In Cp<sub>2</sub>ZrCl<sub>2</sub> system it shows a maximum in the

average rate at 10 mmol of MAO. For the other two, a decrease in MAO decreases the average rate slightly.

GPC study of the polymer samples revealed that the polydispersities were all greater than two, indicating the possibility of the catalysts containing more than one type of active sites. A few papers have reported that immobilization of metallocene catalysts could result in diversifying the characteristics of active sites [Tairova et

al., 1999; Kim et al., 1999]. A kinetic study was then undertaken to examine this possibility. Kinetic models of one and two types of active sites with first and second order catalyst decay were examined. The assumption of two types of sites originated from earlier studies on the heterogeneous Ziegler-Natta catalyst system [Dumas and Hsu, 1989; Tait and Wang, 1988]. The rate equation for catalyst containing two types of active sites can be written as,

$$R_p = [M] \sum_{i=1}^2 k_{p,i} C_i^* \quad (4)$$

where  $R_p$  is the rate of polymerization in g-PE/g-cat/hr,  $[M]$  is the monomer concentration in  $\text{g}/\text{m}^3$  in the polymer particles,  $k_{p,i}$  is the propagation rate constant in  $\text{m}^3/\text{mol}/\text{hr}$  for  $i$ -site, and  $C_i^*$  is the concentration of active sites in  $\text{mol}/\text{g-cat}$  for  $i$ -site. Henry's law was employed to relate the concentration of monomer in the polymer particles to the partial pressure of monomer in gas phase. If the active sites of the catalyst follow the first order decay, the rate equation becomes

$$R_p = [M] \sum_{i=1}^2 k_{p,i} C_{o,i}^* \exp(-k'_{d,i} t) \quad (5)$$

where  $C_{o,i}^*$  is the initial concentration of active sites for  $i$ -site,  $k'_{d,i}$  is the first order catalyst decay constant in  $1/\text{hr}$ , and  $t$  is the polymerization time in hr. Eq. (5) neglects the non-linear effect of ethylene partial pressure on polymerization as shown in the correlation of the average catalyst activities.

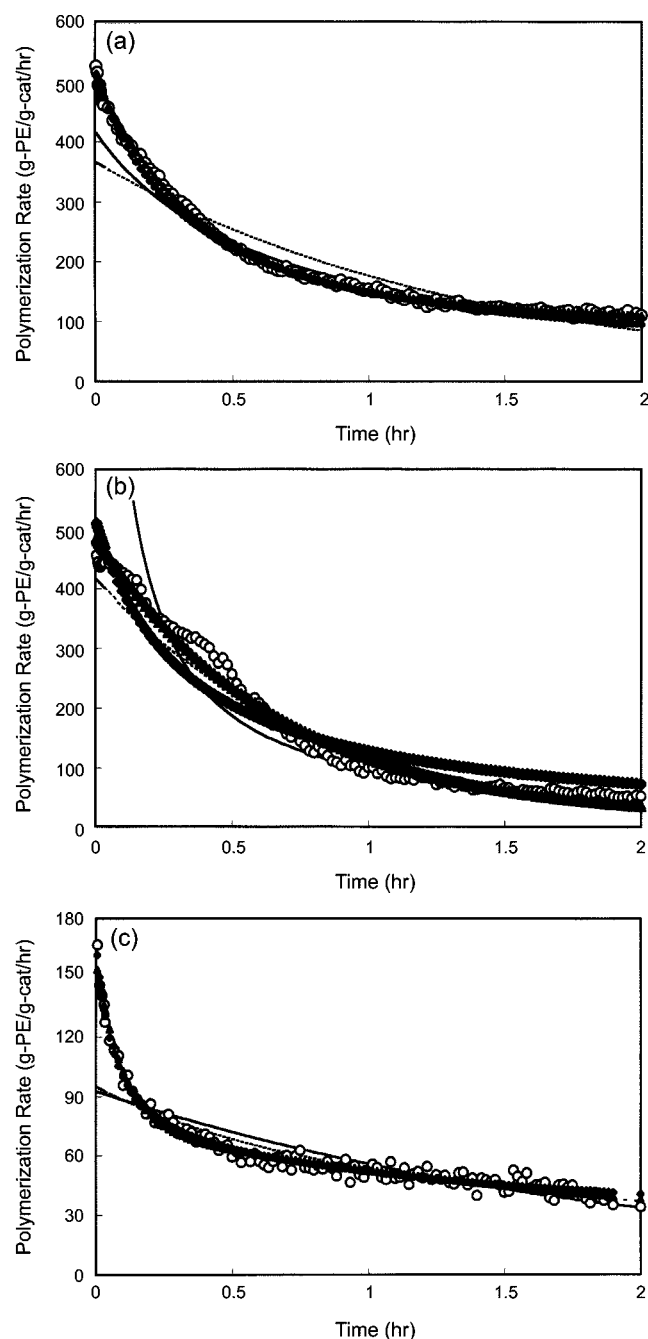
For second order catalyst decay the equation becomes

$$R_p = [M] \sum_{i=1}^2 k_{p,i} C_{o,i}^* / (1 + k''_{d,i} C_{o,i}^* t) \quad (6)$$

where  $k''_{d,i}$  is the second order catalyst deactivation constant in  $\text{g-cat}/\text{mol}/\text{hr}$ .

Although the first order deactivation model is only slightly better fitted to the experimental data than the second order deactivation model as shown in Fig. 2, the fitting results, in general, show overwhelmingly in favor of a two-site model. The standard deviation between the experimental observations and the estimated values was calculated for each run. The residual standard deviations averaged over all experiments are given in Table 3.

When we examined the fitted values of  $k_{p,1} C_{o,1}^*$  and  $k_{p,2} C_{o,2}^*$ , we found on average the ratio of  $k_{p,1} C_{o,1}^* / k_{p,2} C_{o,2}^*$  is 3.7 for  $\text{Cp}_2\text{ZrCl}_2$  catalyst system, 5.1 for  $[\text{Ind}]_2\text{ZrCl}_2$  system, and 2.7 for  $(\text{CH}_3)_2\text{Si}[\text{Ind}]_2\text{ZrCl}_2$  system. The first-order deactivation rate constant,  $k'_{d,i}$  is at least one order of magnitude larger than the second-order deacti-



**Fig. 2.** Typical experimental and model profiles of ethylene polymerization for each catalyst: (a)  $\text{Cp}_2\text{ZrCl}_2$  catalyst system (run 1); (b)  $[\text{Ind}]_2\text{ZrCl}_2$  catalyst system (run 1); (c)  $(\text{CH}_3)_2\text{Si}[\text{Ind}]_2\text{ZrCl}_2$  catalyst system (run 1): experimental ( $\circ$ ); single-site and first-order (---); single-site and second-order (—); dual-site and first-order ( $\blacktriangle$ ); dual-site and second-order ( $\blacklozenge$ ).

**Table 3.** Averaged residual standard deviation<sup>a</sup> for each catalyst

	$\text{Cp}_2\text{ZrCl}_2$	$[\text{Ind}]_2\text{ZrCl}_2$	$\text{Me}_2\text{Si}[\text{Ind}]_2\text{ZrCl}_2$
Single-site first-order	43.000	24.834	24.618
Dual-site first-order	8.346	7.689	7.435
Single-site second-order	40.638	58.025	21.571
Dual-site second-order	16.238	15.643	8.973

<sup>a</sup>defined as  $\sqrt{\sum_{i=1}^n (Y'(i) - Y(i))^2 / (n-2)}$ ,  $Y'(i)$ =experimental value,

$Y(i)$ =calculated value,  $n$ =number of observations, i.e. 120 experimental points.

**Table 4. Average of estimated kinetic parameters for dual site and first order decay**

	$k_{p,1}C_{o,1}^*$ ( $\text{m}^3 \text{ g-cat}^{-1} \text{ h}^{-1}$ )	$k_{p,2}C_{o,2}^*$ ( $\text{m}^3 \text{ g-cat}^{-1} \text{ h}^{-1}$ )	$k_{d,1}$ ( $\text{h}^{-1}$ )	$k_{d,2}$ ( $\text{h}^{-1}$ )
$\text{Cp}_2\text{ZrCl}_2$	0.0964	0.0263	0.2771	0.0127
$[\text{Ind}]_2\text{ZrCl}_2$	0.1212	0.0236	0.0596	0.0040
$\text{Me}_2\text{Si}[\text{Ind}]_2\text{ZrCl}_2$	0.0526	0.0198	0.0829	0.0035

vation rate constant  $k_{d,i}^*$  (Table 4). Thus, the deactivation of the active sites with lower activity is almost negligible, as can be seen from the polymerization rate curves where all curves level off to about the same value, but not zero for a two-hour polymerization.

### CONCLUSIONS

The correlations of the average activities of  $\text{Cp}_2\text{ZrCl}_2$ ,  $[\text{Ind}]_2\text{ZrCl}_2$ , and  $(\text{CH}_3)_2\text{Si}[\text{Ind}]_2\text{ZrCl}_2$  catalysts indicate that temperature is the most important factor affecting the polymerization. The pressure seems to show a negative effect. The MAO level in the range studied has rather weak effect on polymerization.

The kinetic analysis reveals that the catalysts probably contain two types of active sites. The high active sites decay ten times faster than the low active sites.

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